

# AMENDMENTS TO THE CLAIMS

This listing of claims will replace all prior versions, and listings, of claims in the application.

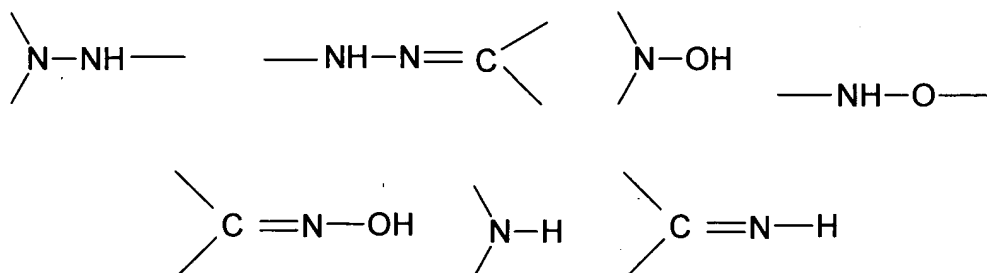
## Listing of Claims:

1-46 (Canceled)

47 - (New) A method of creating a carbon-heteroatom bond by reacting a leaving group-bearing unsaturated compound and a nucleophilic compound introducing a heteroatom which can substitute for the leaving group, thereby creating a carbon-heteroatom bond, in the presence of a palladium-based catalyst, optionally a ligand, said reaction taking place in the presence of an effective amount of a metal hydroxide or ammonium hydroxide, associated with an alcohol solvent.

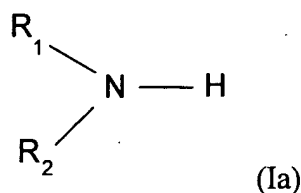
48 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate is an organic hydrocarbon compound acyclic or cyclic having at least one oxygen atom and/or at least one nitrogen atom bearing a free doublet: optionally said nitrogen atom to be introduced by means of a functional group, or included in a ring, optionally having 3 to 8 atoms, in the form of NH.

49 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate has at least one atom or group below:



50 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate is a primary amine, a secondary amine; an imine; an oxime; a hydroxylamine; a hydrazine; a hydrazone or a nitrogenous heterocycle.

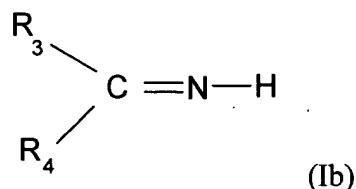
51 - (New) The method as claimed in claim 1, wherein the nucleophilic substrate corresponds to the formula below:



wherein:

- $R_1$  and  $R_2$  represent, independently of one another, a hydrogen atom or a hydrocarbon group having from 1 to 20 carbon atoms, optionally a linear or branched, saturated or unsaturated, acyclic aliphatic group; a monocyclic or polycyclic, saturated, unsaturated or aromatic carbocyclic or heterocyclic group; a chain of the abovementioned groups,
- at most one of the groups  $R_1$  and  $R_2$  represents a hydrogen atom.

52 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate corresponds to the formula below:



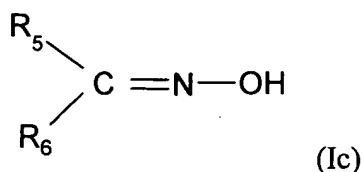
wherein:

- $R_3$  and  $R_4$ , which are identical or different, have the meaning given for  $R_1$  and

R<sub>2</sub> in formula (Ia),

- at most one of the groups R<sub>3</sub> and R<sub>4</sub> represents a hydrogen atom.

53 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate corresponds to the formula below:



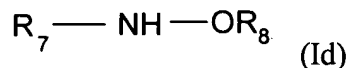
wherein:

- R<sub>5</sub> and R<sub>6</sub>, which are identical or different, have the meaning given for R<sub>1</sub> and

R<sub>2</sub> in formula (Ia),

- at most one of the groups R<sub>5</sub> and R<sub>6</sub> represents a hydrogen atom.

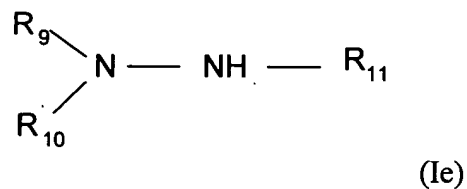
54 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate corresponds to the formula below:



wherein:

- R<sub>7</sub> has the meaning given for R<sub>1</sub> and R<sub>2</sub> in formula (Ia) with the exception of a hydrogen atom,
- R<sub>8</sub> represents a hydrogen atom, a linear or branched, saturated or unsaturated, acyclic aliphatic group; a monocyclic or polycyclic, saturated or unsaturated carbocyclic group; a chain of the abovementioned groups.

55 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate corresponds to the formula below:

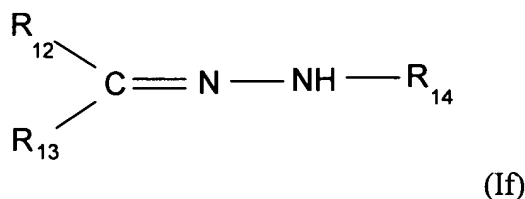


wherein:

-  $R_9$ ,  $R_{10}$  and  $R_{11}$ , which may be identical or different, have the meaning given for  $R_1$  and  $R_2$  in formula (Ia).

- $R_{11}$  represents a hydrogen atom or a protective group G,
- at most one of the groups  $R_9$  and  $R_{10}$  represents a hydrogen atom,
- or else  $R_9$  and  $R_{10}$  may be linked so as to constitute, with the carbon atoms that bear them, a monocyclic or polycyclic, saturated, unsaturated or aromatic, carbocyclic or heterocyclic group having from 3 to 20 atoms.

56 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate corresponds to the formula below:



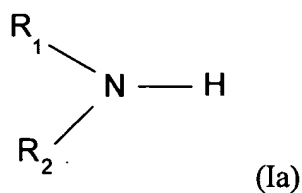
whwrein:

-  $R_{12}$ ,  $R_{13}$  and  $R_{14}$ , which are identical or different, have the meaning given for  $R_1$  and  $R_2$  in formula (Ia),

- at most one of the groups  $R_{12}$  and  $R_{13}$  represents a hydrogen atom, or

50 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate is a primary amine, a secondary amine; an imine; an oxime; a hydroxylamine; a hydrazine; a hydrazone or a nitrogenous heterocycle.

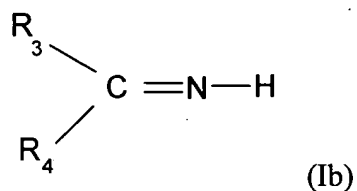
51 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate corresponds to the formula below:



wherein:

- $\text{R}_1$  and  $\text{R}_2$  represent, independently of one another, a hydrogen atom or a hydrocarbon group having from 1 to 20 carbon atoms, optionally a linear or branched, saturated or unsaturated, acyclic aliphatic group; a monocyclic or polycyclic, saturated, unsaturated or aromatic carbocyclic or heterocyclic group; a chain of the abovementioned groups,
- at most one of the groups  $\text{R}_1$  and  $\text{R}_2$  represents a hydrogen atom.

52 - (New) The method as claimed in claim 47, wherein the nucleophilic substrate corresponds to the formula below:



wherein:

- $\text{R}_3$  and  $\text{R}_4$ , which are identical or different, have the meaning given for  $\text{R}_1$  and

comprising a leaving group Y corresponds to formula (II):



in said formula (II):

- R<sub>0</sub> represents a hydrocarbon group having from 2 to 20 carbon atoms and has a double bond or a triple bond located in the α-position with respect to a leaving group Y or a monocyclic or polycyclic, aromatic carbocyclic and/or heterocyclic group bearing a leaving group on one ring.

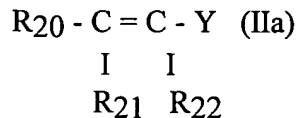
61 - (New) The method as claimed in claim 60, wherein the unsaturated compound comprising a leaving group corresponds to formula (II) wherein:

- R<sub>0</sub> represents an aliphatic hydrocarbon group having a double bond or a triple bond in the α-position with respect to the leaving group or an unsaturated cyclic hydrocarbon group in which an unsaturation bears the leaving group,
- R<sub>0</sub> represents a monocyclic or polycyclic, aromatic carbocyclic and/or heterocyclic group, and
- Y represents a leaving group, optionally a halogen atom or a sulfonic ester group of formula -OSO<sub>2</sub>-R<sub>e</sub>, in which R<sub>e</sub> is a hydrocarbon group.

62 - (New) The method as claimed claim 60, wherein the unsaturated compound comprising a leaving group corresponds to formula (II) in which Y represents a bromine or chlorine atom or a sulfonic ester of formula -OSO<sub>2</sub>-R<sub>e</sub>, in which R<sub>e</sub> is a linear or branched alkyl group having from 1 to 4 carbon atoms, optionally a methyl, ethyl, a phenyl, tolyl or a trifluoromethyl group.

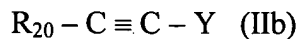
63 - (New) The method as claimed in claim 60, wherein the unsaturated compound comprising a leaving group corresponding to formula (II) is:

- (1) an aliphatic compound bearing a double bond that can be represented by formula (IIa):



in said formula (IIa):

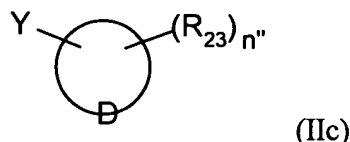
- R<sub>20</sub>, R<sub>21</sub> and R<sub>22</sub>, which are identical or different, represent a hydrogen atom or a hydrocarbon group having from 1 to 20 carbon atoms, which is a linear or branched, saturated or unsaturated aliphatic group; a monocyclic or polycyclic, saturated, unsaturated or aromatic, carbocyclic or heterocyclic group; or a chain of aliphatic and/or carbocyclic and/or heterocyclic groups as mentioned above, and
  - Y symbolizes the leaving group as defined above,
- (2) an aliphatic compound bearing a triple bond and that can be represented by formula (IIb):



in said formula (IIb):

- R<sub>20</sub> has the meaning given in formula (IIa), and
- Y represents a leaving group as defined above,

- (3) an aromatic compound subsequently referred to as "haloaromatic compound" and that can be represented by formula (IIc):



wherein:

- D symbolizes the residue of a ring forming all or part of a monocyclic or polycyclic, aromatic carbocyclic and/or heterocyclic system,
- R<sub>23</sub>, which is identical or different, represents substituents on the ring,
- Y represents a leaving group as defined above, and
- n'' represents the number of substituents on the ring.

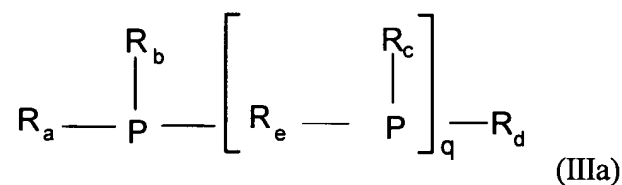
64 - (New) The method as claimed in claim 60, wherein the leaving group-bearing compound corresponding to formula (II) is vinyl chloride, vinyl bromide, bromoalkyne, iodoalkyne,  $\beta$ -bromostyrene,  $\beta$ -chlorostyrene, p-chlorotoluene, p-bromoanisole or p-bromotrifluorobenzene.

65 - (New) The method as claimed in claim 47, wherein the catalyst comprises the metal element Pd introduced in the form of a finely divided metal, in the form of an inorganic derivative such as an oxide or a hydroxide; in the form of a mineral salt, optionally nitrate, sulfate, oxysulfate, halide, oxyhalide or carbonate; in the form of an organic derivative, optionally cyanide, oxalate, acetylacetonate; alkoxide, methoxide or ethoxide; carboxylate, acetate, or in the form of a complex, optionally a chlorinated or cyanated complex of Pd metals and/or of alkali metals, optionally sodium or potassium, or of ammonium.

66 - (New) The method as claimed in claim 65, wherein the Pd element is introduced through palladium chloride, palladium acetate or palladium-on-charcoal.

67 - (New) The method as claimed in claim 47, wherein the ligand is a phosphine, a phosphite or a phosphonite.

68 - (New) The method as claimed in claim 67, wherein the phosphine corresponds to the formula below:



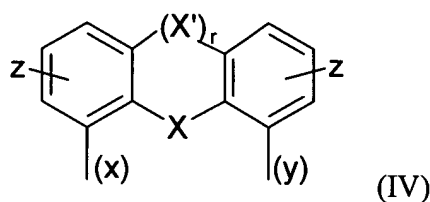
in said formula:

- q is equal to 0 or 1,
- the groups  $\text{R}_a$ ,  $\text{R}_b$ ,  $\text{R}_c$  and  $\text{R}_d$ , which are identical or different, represent:
  - . an alkyl group having from 1 to 12 carbon atoms,
  - . a cycloalkyl group having 5 or 6 carbon atoms,
  - . a cycloalkyl group having 5 or 6 carbon atoms, which is substituted with one or more alkyl groups having 1 to 4 carbon atoms, or alkoxy groups having 1 or 4 carbon atoms,
  - . a phenylalkyl group in which the aliphatic portion contains from 1 to 6 carbon atoms,
  - . a phenyl or biphenyl group,
  - . a phenyl or biphenyl group substituted with one or more alkyl groups having

from 1 to 4 carbon atoms or alkoxy groups having from 1 to 4 carbon atoms,  
one or more halogen atoms, or a trifluoromethyl group,

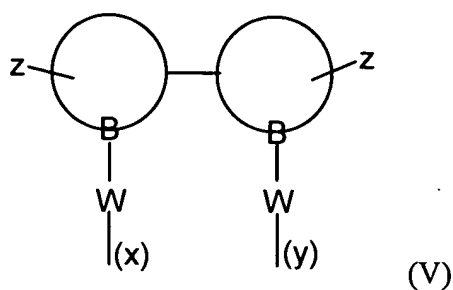
- the group  $R_e$  represents:

- . a valency bond or a saturated or unsaturated, linear or branched divalent hydrocarbon group having from 1 to 6 carbon atoms,
- . an aromatic group of formula:



in which:

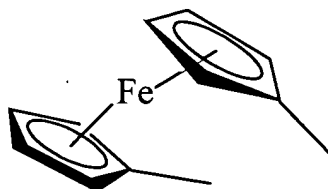
- ✧ Z represents a hydrogen atom, an alkyl group having from 1 to 10 carbon atoms, a halogen atom or a trifluoromethyl group,
  - ✧ X is an oxygen or sulfur atom or a linear or branched alkylene group having from 1 to 3 carbon atoms,
  - ✧ if r is equal to 1, X' represents a valency bond, an oxygen, sulfur or silicon atom or a linear or branched alkylene group having from 1 to 3 carbon atoms,
  - ✧ if r is equal to 0, the two rings are not linked,
  - ✧ (x) and (y) pinpoint respectively the two bonds established between the group  $R_e$  symbolized by formula (IV) and the phosphorus atoms,
- . an aromatic group of formula:



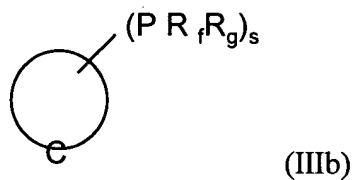
in which:

- ✧ Z has the meaning given above,
- ✧ B represents the residue of a benzene or naphthalene ring,
- ✧ W represents a valency bond or a linear or branched alkylene group having from 1 to 3 carbon atoms,
- ✧ (x) and (y) pinpoint respectively the two bonds established between the group  $R_e$  symbolized by formula (V) and the phosphorus atoms,

a ferrocene group of formula:



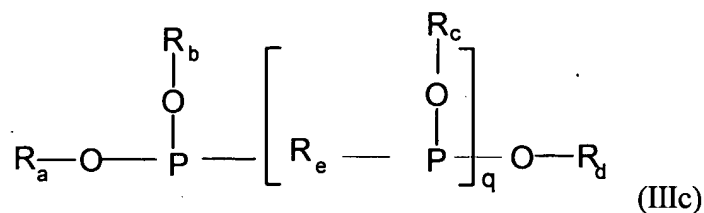
69 - A method as claimed in claim 67, wherein the phosphine corresponds to the formula below:



in which:

- ✧ C represents the residue of a pentane or cyclohexane ring,
- ✧  $R_f$  and  $R_g$ , which may be identical or different, have the meaning given for  $R_a$  or  $R_b$ , in formula (IIIa), and
- ✧ s is a number equal to 1 to 6, preferably equal to 4.

70 - (New) The method as claimed in claim 67, wherein the phosphonite corresponds to the formula below:



in said formula, the groups  $R_a$ ,  $R_b$ ,  $R_c$ ,  $R_d$  and  $R_e$ , and the symbol q have the meaning given for formula (IIIa).

71 - (New) The method as claimed in claim 67, wherein the ligand is:  
tricyclohexylphosphine, trimethylphosphine, triethylphosphine, tri-*n*-butylphosphine, triisobutylphosphine, tri-*tert*-butylphosphine, tribenzylphosphine, dicyclohexylphenylphosphine, 2-dicyclohexylphosphino-2-methylbiphenyl, triphenylphosphine, dimethylphenylphosphine, diethylphenylphosphine, di-*tert*-butylphenylphosphine, tri(*p*-tolyl)phosphine, isopropylidiphenylphosphine, tris(pentafluorophenyl)phosphine, tri(*o*-tolyl)phosphine, bisdiphenylphosphinomethane, bisdiphenylphosphinoethane, bisdiphenylphosphinopropane, bisdiphenylphosphinobutane, bisdiphenylphosphinopentane, bisdiphenylphosphinoferrocene, 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP), bis-[(2-diphenylphosphino)phenyl] ether (DPEPHOS), 4,5-bis(diphenylphosphino)-9,9-

dimethylxanthene (XANTPHOS), or tetrakis-(2,4-di-tert-butylphenyl)-4,4'-diphenylenebisphosphonite.

72 - (New) The method as claimed in claim 47, wherein the base is an ammonium hydroxide or a hydroxide of a monovalent metal and/or of a bivalent metal, optionally an alkali and/or alkaline earth metal, introduced in a solid form or in a solution.

73 - (New) The method as claimed in claim 47, wherein the solvent is a monoalcohol, a polyalcohol, an ether alcohol or an amino alcohol.

74 - (New) The method as claimed in claim 73, wherein the alcohol is a primary alcohol or secondary alcohol that is hindered or a tertiary alcohol, said alcohol corresponds to the formula below:



in said formula (VI):

- $R_h$  represents an optionally substituted hydrocarbon group having from 1 to 24 carbon atoms, which is a linear or branched, saturated or unsaturated acyclic aliphatic group; a monocyclic or polycyclic, saturated or unsaturated cycloaliphatic group; or a linear or branched, saturated or unsaturated aliphatic group bearing a cyclic substituent.

75 - (New) The method as claimed in claim 74, wherein the solvent is n-butanol, tert-butanol, ethylene glycol, N,N-dimethylethanolamine; methoxyethanol, 1-methoxypropan-2-ol, or tert-amyl alcohol.

76 - (New) The method as claimed in claim 72, wherein a reactive milling of the metal hydroxide or ammonium hydroxide and of the alcohol is carried out.

77 - (New) The method as claimed in claim 72, wherein a reactive milling of sodium hydroxide (already milled or in the form of pellets) and of tert-amyl alcohol or tert-butanol is carried out.

78 - (New) The method as claimed in claim 47, wherein the compound introducing the Pd element, is used in an amount, expressed by the molar ratio of the number of moles of said Pd compound to the number of moles of compound of formula (II), ranges between 0.005 and 1, optionally between 0.01 and 0.1.

79 - (New) The method as claimed in claim 47, wherein the alcohol-type solvent is further combined with a co-solvent which is an apolar aprotic solvent.

80 - (New) The method as claimed in claim 79, wherein the apolar aprotic solvent is an aliphatic, cycloaliphatic or aromatic hydrocarbon, optionally hexane, cyclohexane, methylcyclohexane, or petroleum ether cuts; an aromatic hydrocarbon, optionally benzene, toluene, xylenes, cumene, mesitylene, or petroleum cuts consisting of a mixture of alkylbenzenes.

81 - (New) The method as claimed in 79, wherein the co-solvent is used in an amount representing from 1 to 50% of the volume of the alcohol solvent, optionally from 10 to 20%.

82 - (New) The method as claimed in claim 47, wherein the coupling reaction between the nucleophilic compound and the leaving group-bearing unsaturated compound takes place at a temperature which is chosen such that the reactants are maintained in the liquid state.

83 - (New) The method as claimed in claim 82, wherein the temperature is situated

between 50°C and 200°C, optionally between 90°C and 110°C.

84 - (New) The method as claimed in claim 47, wherein the leaving group-bearing unsaturated compound, the base, the alcohol solvent are loaded; the compound introducing the Pd metal element and the ligand or else the preformed metal complex are added separately to the medium; the reaction medium is brought to the selected reaction temperature; the nucleophilic compound, is subsequently added and the coupling product obtained is then recovered.

85 - (New) The method as claimed in claim 47, wherein the coupling product obtained is benzophenone N-p-tolylhydrazone, benzophenone N-phenylhydrazone, benzophenone N-p-methoxyphenylhydrazone, benzophenone N-o-tolylhydrazone, benzophenone N-p-fluorophenylhydrazone, benzophenone N-4-fluoro-3-chlorophenylhydrazone, benzophenone N-2-fluoro-5-chlorophenylhydrazone, or benzophenone N-4-fluoro-3-cyanophenylhydrazone.